

UNITED STATES ATOMIC ENERGY COMMISSION

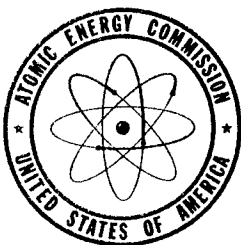
AECD-3187

THE USE OF THE PAPER COLUMN SEPARATION
IN THE ESTIMATION OF MICROGRAM QUANTITIES
OF URANIUM

By
Richard H. Kennedy

June 7, 1950

Mineral Engineering Laboratory
Massachusetts Institute of Technology



EXEMPTION CATEGORY A

Approved for public release
Distribution Unlimited

Technical Information Service, Oak Ridge, Tennessee

19970107 021

DTIC QUALITY INSPECTED 1

ATI No. 163532
ASTIA FILE COPY
S-T-1

ABSTRACT

By combining the paper column separation with a microvolumetric, colorimetric, or fluorimetric method for determining uranium the quantitative estimation of small concentrations of uranium in the presence of large concentrations of other elements has been simplified. As little as 5.3×10^{-7} grams of uranium as U_3O_8 has been separated quantitatively on the column prior to fluorimetric determination.

CHEMISTRY

Issuance of this document does not constitute authority for declassification of classified copies of the same or similar content and title and by the same author.

Reproduced direct from copy
as submitted to this office.

Work performed under
Contract No. W-7405-eng-85.

This report is based in MITG-A84.

PRINTED IN USA
PRICE 10 CENTS

THE USE OF THE PAPER COLUMN SEPARATION IN THE ESTIMATION OF
MICROGRAM QUANTITIES OF URANIUM*

By Richard H. Kennedy

I. INTRODUCTION

In connection with the testing of the efficiency of various processes for the extraction of uranium from ores and ore products, samples are often encountered of extremely low uranium content. Sometimes it is satisfactory for the analytical laboratory to report the uranium content of these barren materials simply as less than 0.001 per cent U_3O_8 , or less than 0.001 gram per liter U_3O_8 . Frequently, however, it is desirable to obtain a reasonably accurate quantitative determination of uranium at these low concentrations. Sometimes these barren samples can be analyzed fluorimetrically without the need of chemical separations. Often, however, quenching elements are present in sufficient concentration so that the low dilution ratio allowed by the small uranium content of the samples does not eliminate quenching. The usual practice has been to separate the uranium from these materials by an ether extraction, employing the conventional liquid-liquid type extractor^{1/}. This method works well, but is time consuming. In an attempt to improve this situation, the paper chromatographic method developed by the Chemical Research Laboratory, Teddington, Middlesex^{2,3,4,5,6/}, was combined with a fluorimetric final determination to give a more rapid quantitative analytical method on microgram quantities of uranium. With larger amounts of uranium, the paper column separation has been followed by a microvolumetric or colorimetric method for uranium determination.

In the paper chromatographic method, the uranium in aqueous solution containing free nitric acid is adsorbed on partially nitrated cellulose packed in a glass column. The adsorbed uranium is then selectively extracted from the column with diethyl ether containing nitric acid. The uranium in the solvent is then determined fluorimetrically, although other methods such as colorimetric or volumetric can also be used.

^{1/} References are given in Appendix B.

*Work performed under Contract No. W-7405-Eng-85

The main point that had to be established in applying the paper column separation to samples of low uranium content was whether or not the separation was satisfactory first with milligram quantities and then with microgram quantities of U_3O_8 .

The test work that was done to establish the quantitative separation of small amounts of uranium from elements that interfere with the fluorimetric method is presented in this report. This work was started in February, 1949, but was not completed until April, 1950.

II. SUMMARY

The paper column method for the separation of uranium from a variety of samples as described in a series of reports from the Chemical Research Laboratory, Teddington, Middlesex, has been combined with a final fluorimetric determination to give a rapid analytical method for samples containing about 1 ppm of uranium. Several modifications of apparatus and procedure have been made which considerably increase the speed of the paper column method.

III. MATERIALS AND METHODS

Apparatus

The glass extraction tube is shown in Figure 1A. It differs from the tube recommended by the British (Figure 1B) in that the top of the tube is straight-sided instead of funnel-shaped. It was found difficult to control the rate of flow of the solvent through the paper column as described in the British reports. While the stopcock could be used to slow down the rate of flow of the ether when necessary, there was no way by which it could be speeded up. When a longer-than-average wad was packed into the column for the extraction of a large sample, the ether flow rate was far slower than required for a clean separation of the uranium. The straight-sided top on the modified column allows a stopper with a compressed-air line and a vent to be placed on the top of the column. Compressed air is fed from a manifold to a number of tubes simultaneously as shown in Figure 2. Variation of the ether flow rate at will is thus made possible. Compressed air is also blown into the beakers receiving the column effluents, thus evaporating most of the ether from the beakers while the extraction is in progress, and saving time in subsequent removal of ether on the steam bath.

Pulp Preparation^{3/}

About 100 grams of Whatman No. 1 filter paper is broken to a pulp in water (roughly 25 ml of water per gram of paper) either by a minimum of agitation in a Waring Blendor or by gentle shaking on a Burrel Wrist Action Shaker for about 2 hours. The latter instrument is preferred as its action on the fibers is less severe. The pulp is then sucked dry on a Buechner funnel and transferred to a 4-liter beaker containing 2 liters of boiling 5 per cent nitric acid. The boiling is continued for 10 minutes, and the pulp is filtered, washed with 2 liters of distilled water, 1 liter of absolute alcohol, and 2 liters of ether. After the pulp is nearly free of ether, it is broken up fairly fine by hand. The slightly ether-damp pulp is then placed in a Waring Blendor jar (about 5 grams at a time), and the switch is snapped on and off a few times. The blendor jar is then shaken by hand to shift the pulp near the blades. When this process is repeated a few times, most of the lumps, which so annoyingly impede the rapid and smooth packing of a column, are eliminated. The pulp is separated to a light and fluffy consistency and is then stored in a jar with a tightly fitting cover so that it may be kept slightly damp with ether.

Preparation of Extraction Tubes^{3,7/}

About 1 gram of Silicone stopcock grease is dissolved in 100 ml of carbon tetrachloride. This solution is used to coat the inside of the clean, dry extraction tube. The excess is run off and the carbon tetrachloride evaporated. Before use the column is rinsed a few times with ether. The coating is good for about 6 extractions before it must be renewed. Silicone grease is also used to lubricate the stopcock.

Column Preparation

It is essential for good extraction to form in the column a smooth wad of nitrated cellulose free from lumps and air spaces. The column is first half filled with the solvent (anhydrous freshly distilled ether containing 5 per cent concentrated nitric acid by volume). Roughly 0.5 gram of pulp is added and agitated by a rapid up-and-down motion of the glass plunger (Figure 1C) until the pulp is completely broken up. It is then gently pressed down into the bottom of the column. More pulp is added and the process repeated until a wad of the desired height is built up. Column heights of 2 to 5 inches are commonly used, depending on the volume of the sample to be extracted and the technique used in putting the sample on the column. Before use the column is extracted with 100 ml of solvent at a flow rate of approximately 5 ml per minute.

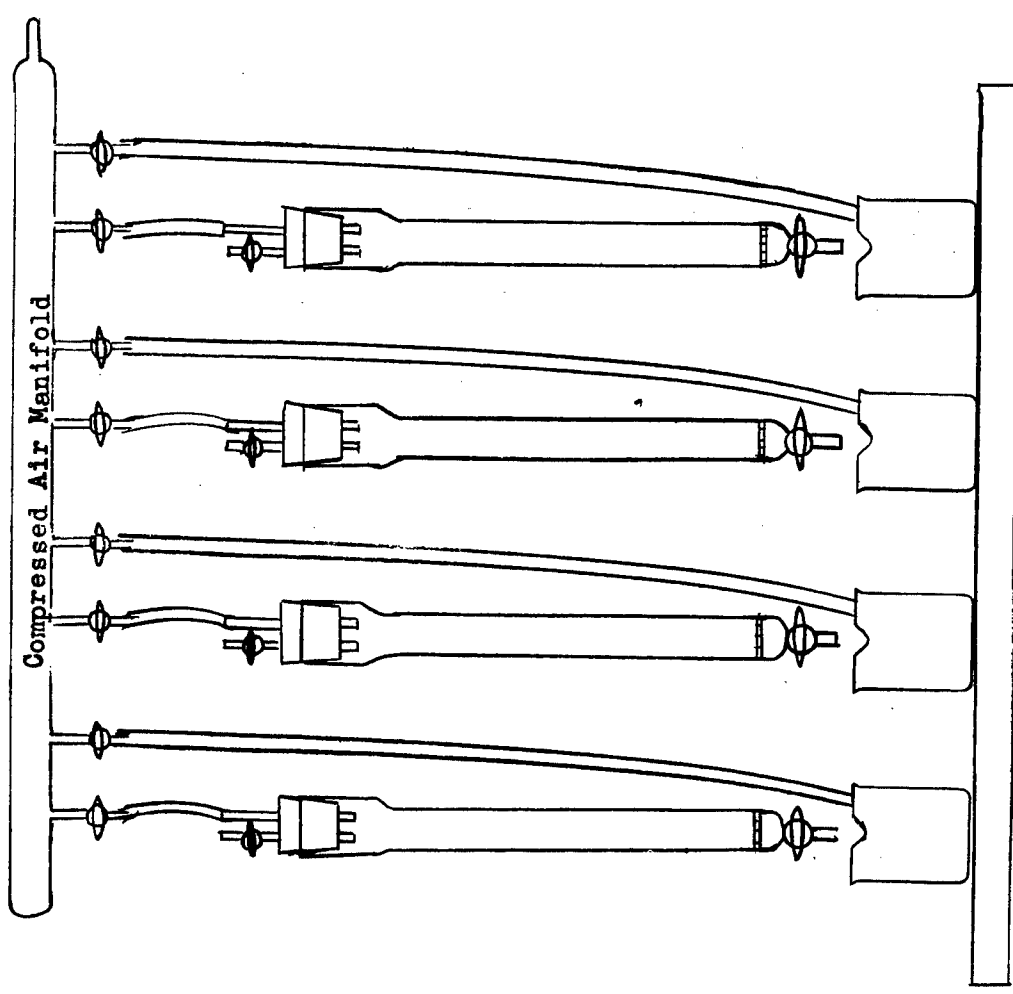


Figure 2. Multiple Unit Assembly

Note: Perforated porcelain plates used in A and B.
 Diameters: A = 2.2 cm;
 B = 2.0 cm; C = 9 mm.

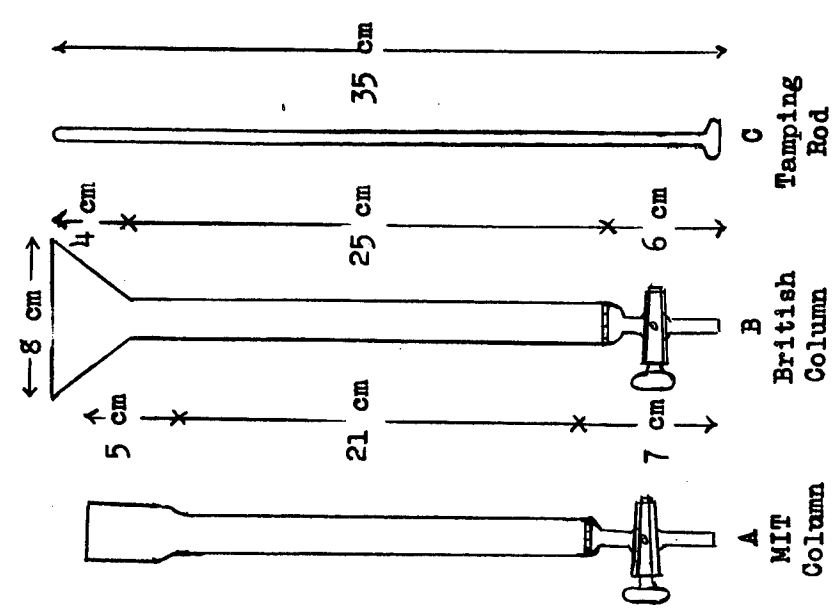


Figure 1. Paper Column Apparatus

Method of Uranium Determination

While many other methods can be used for the determination of the uranium in the effluent from the cellulose column, the fluorimetric method offers several advantages not enjoyed by any other method published to date. The method is well suited for routine work, as large numbers of samples can be analyzed rapidly. The chief advantage of the fluorimetric method lies in the fact that its high sensitivity makes possible the quantitative determination of submicrogram quantities of uranium. This enables the analyst to start with much smaller samples than would otherwise be possible. This factor becomes increasingly important as the uranium content of the samples diminishes, particularly if a fusion is required to put the sample into solution. The fluorimetric method has a 7 per cent standard deviation. This precision is usually sufficient on samples of low uranium content.

Three different fluorimeters were used in the investigative work on the paper column. The Y-12 Model R^{8,9,10/}, the Price-Argonne^{11,12,13/}, and MIT Model 1 (Report MITG-A70, in preparation). The MIT Model 1 fluorimeter is now used routinely for uranium analysis. It has about ten times the sensitivity of the Price-Argonne instrument. During the investigation of variations in the column extraction procedure, the peroxide-colorimetric method and the microvolumetric method were used for uranium determination. The colorimetric method proved to have no advantage over the fluorimetric method. The microvolumetric method, which has a standard deviation of 3 to 5 per cent is valuable as a check on the fluorimetric analyses, and where precision is of primary importance. For a final determination on the MIT Model 1 fluorimeter, the uranium content of the sample is adjusted to 0.0001 to 0.002 gram per liter U_3O_8 . As a 5-ml volumetric flask is the smallest convenient size in which to make the final dilution of the sample, the sample should contain a minimum of 0.5 microgram of U_3O_8 . For routine work it is desirable to have at least 10 micrograms of uranium in the sample. The Price-Argonne fluorimeter requires a final dilution of 0.0002 to 0.002 gram per liter of U_3O_8 . For determination on the Model R fluorimeter, a solution containing 0.00025 to 0.1 gram per liter of U_3O_8 is required. From 0.5 to 5.0 micrograms of uranium is required per determination, so that it is desirable to have at least 20 micrograms of uranium in the sample. For either the colorimetric or the microvolumetric method, 0.1 mg of U_3O_8 is the minimum required for accurate quantitative analysis; 0.3 to 3.0 mg U_3O_8 per sample is preferred.

A summary of the methods for final determination of the uranium is given in Appendix A.

IV. ANALYTICAL PROCEDURE

A. Solution of Solid Samples.

Conventional methods are used in this laboratory for the solution of the uranium from solid samples. No single method of attack has been found which is equally efficient for all types of materials. A 2-hour boil with 50 per cent nitric acid quantitatively extracts uranium from siliceous ores and products. Phosphate rock is not reliably extracted with nitric acid and requires either a preliminary treatment with hydrofluoric acid or a potassium hydroxide fusion. Monazites are most conveniently handled by the sodium-peroxide fusion method of Seeyle and Rafter^{14,15,7/}. Some pitchblende ores require the elimination of arsenic before paper column separation^{6,7/}.

Sulfate, chloride, and phosphate^{5/} interfere with the column extraction of uranium. The methods for the elimination of these interferences are as follows:

- 1) When chlorides are present 0.5 ml of sulfuric acid is added to the sample in a 50-ml beaker. The sample is fumed almost to dryness. The beaker is cooled, washed down with water, 5 ml of 1:1 nitric acid added, and evaporated to dryness. The residue is taken up by boiling with 5 ml of 25 per cent nitric acid. One ml of a saturated solution of barium nitrate in 25 per cent nitric acid is added to the sample, which is then ready for extraction. The precipitate is not removed from the sample.
- 2) If the sample contains sulfates but not chlorides, 5 ml of 1:1 nitric acid is added, and the sample evaporated to dryness. The residue is taken up in 25 per cent nitric acid and any remaining sulfate precipitated with barium nitrate as described above.
- 3) Interference from phosphate ion is eliminated by complexing with ferric nitrate. A saturated solution of ferric nitrate in 25 per cent nitric acid is added dropwise until the straw color persists.

B. Column Extraction.

When the uranium content of the sample is sufficiently high, the sample is transferred to a 10- or 25-ml volumetric flask, the nitric acid content adjusted to 25 to 35 per cent, and an aliquot of 1, 2, or 5 ml is pipetted directly onto the prepared cellulose column. If the uranium content of the sample is too low to permit this dilution (under 10 micrograms U_3O_8), the whole sample is reduced to a volume of 5 ml or less and poured from the beaker directly onto the column. The column is then eluted with 100 ml of anhydrous ether containing 5 per cent

nitric acid at a flow rate of 5 ml per minute in 10-ml portions, each portion being first poured into the beaker which contained the sample. The eluate from the column is caught in a 150-ml beaker containing about 25 ml of water. The ether is evaporated off on a steam bath, and the aqueous uranium solution is transferred to a volumetric flask. The uranium is determined fluorimetrically by the procedure described in Report MITG-A65. (See Appendix A)

If the sample is too high in salt content to permit evaporation to 5 ml or less, the sample may be adsorbed first on dry pulp while still in the beaker before being transferred to the column. Dry pulp is mixed with the sample until the sample is completely absorbed. The pulp is transferred with the aid of a glass rod to the column and pressed down with the plunger to form a continuation of the previously prepared wad.

If the volume of the sample prior to extraction on the paper column is kept down to 5 ml or less, 3 successive samples can be extracted on the same column, if a fluorimetric or colorimetric final determination is used. This greatly reduces the time required for column preparation. One sample is poured on the column and extracted, then another sample is poured on the same column and likewise extracted, etc. The column may be used for additional samples until the aqueous layer comes within 2 inches of the bottom of the column, or until it is obvious that the addition of more ether will cause impurities to start coming off the column. Even if small amounts of impurities do appear in the eluate, they will not affect the fluorimetric determination of the uranium. This procedure of multiple extractions on a single column was tested on known samples by fluorimetric, colorimetric, and microvolumetric methods. Quantitative results were obtained by fluorimetric and colorimetric methods. Results by the microvolumetric method tended to be high after the first extraction.

V. EXPERIMENTAL DATA

A. Successive Extractions on a Single Column.

To find out whether or not more than one sample could be extracted on a column, a set of siliceous ore samples of accurately determined uranium content were leached with nitric acid, and the filtrates were extracted successively on a single column. Samples from three columns were analyzed colorimetrically. The results are given in Table 1. The samples were alternated with spikes of pure uranyl nitrate so that the appearance of interferences could be more readily ascertained. The results are well within the expected accuracy of the colorimetric method, which has a standard deviation of about 7 per cent.

Table 1. Multiple Extractions on a Column - Colorimetric
Determination of Uranium

Sample	Column	Order of Extraction	U ₃ O ₈ Contained mg/Sample	U ₃ O ₈ Determined mg/Sample	Per Cent Error
37G3*	A	1	0.75	0.80	+6.7
Spike**	A	2	0.47	0.47	0.0
37G3	A	3	0.75	0.75	0.0
Spike**	A	4	0.47	0.44	-6.4
37G3	A	5	0.75	0.79	+5.3
52G3*	B	1	0.295	0.32	+8.5
Spike**	B	2	0.47	0.48	+2.1
37G3	B	3	0.75	0.75	0.0
Spike**	B	4	0.47	0.47	0.0
37G3	B	5	0.75	0.82	+9.3
52G3	C	1	0.295	0.305	+3.4
54G2*	C	2	0.285	0.26	-8.8
52G3	C	3	0.295	0.34	+15.0
54G2	C	4	0.285	0.285	0.0

* 5-gram samples of acid leach residues from siliceous ores.

** 0.5 ml of uranyl nitrate solution containing 0.94 g/l uranium as U₃O₈.

Samples from 4 columns were analyzed microvolumetrically. The data given in Table 2 show that the results are high and erratic and tend to become progressively higher after the first sample has been extracted.

Table 2. Multiple Extractions on a Column - Microvolumetric Determination of Uranium

Sample	Column	Order of Extraction	U ₃ O ₈ Contained mg/Sample	U ₃ O ₈ Determined mg/Sample	Per Cent Error
37G3	A	1	0.75	0.82	+9.3
Spike	A	2	1.00	1.06	+6.0
37G3	A	3	0.75	1.03	+37
Spike	A	4	1.00	1.04	+4.0
37G3	A	5	0.75	1.00	+33
54G2	B	1	0.285	0.30	+5.3
Spike	B	2	1.00	1.06	+6.0
54G2	B	3	0.285	0.32	+12
Spike	B	4	1.00	1.05	+5.0
54G2	B	5	0.285	0.33	+17.5
54G2	C	1	0.285	0.296	+3.9
37G3	C	2	0.75	0.818	+9.1
54G2	C	3	0.285	0.348	+22.
37G3	C	4	0.75	0.995	+33
54G2	C	5	0.285	0.432	+52.
37G3	D	1	0.75	0.627	-16.
54G2	D	2	0.285	0.488	+71.
37G3	D	3	0.75	0.821	+9.5
54G2	D	4	0.285	0.398	+40.
37G3	D	5	0.75	0.824	+9.9

The high results are probably caused by the extraction of iron. The multiple-extraction technique is not applicable if the uranium is to be determined volumetrically.

The microvolumetric method may be used satisfactorily for the determination of the uranium from column separations if only one sample is placed on a column. To establish this point, four 0.1000-gram portions of a sample were weighed out, dissolved in nitric acid, and extracted on separate columns. After removal of the ether, the aqueous solutions of the samples were diluted to 500 ml. A 10-ml aliquot of each sample was evaporated with sulfuric acid to remove the nitric acid. A cupferron separation was then performed on 2 of the samples, and the 4 samples then determined microvolumetrically. The results given in Table 3 show good agreement between the samples analyzed with and without the cupferron separation.

Table 3. One Sample Per Column - Microvolumetric Determination

Sample	Cupferron Step	mg U ₃ O ₈ in Aliquot
P4007	Yes	0.687
P4007	Yes	0.706
P4007	No	0.697
P4007	No	0.706

Various 3-gram samples of phosphate rock were decomposed with nitric and hydrofluoric acids. The samples were then evaporated to dryness to remove the HF, redissolved in nitric acid and diluted to 250 ml. One portion of each sample when analyzed on the Argonne fluorimeter showed quenching. A second portion of each sample when rediluted 1:5 and run on the MIT Model 1 instrument showed no quenching and gave higher results. A third portion of each sample was paper-column extracted and analyzed on the MIT-1, the Argonne, and the Model R Fluorimeters. Data are given in Table 4.

Table 4. Multiple Extraction on a Column - Fluorimetric Determination

Sample No.	Direct Fluorimetric Analysis*, % U ₃ O ₈		Column	Fluorimetric After Column Separation, % U ₃ O ₈		
	Argonne	MIT		Argonne	MIT	Model R
E 10152	--	0.0097	A	0.010	0.0097	0.0099
E 4160	0.0110	0.014	A	0.013	0.014	0.014
E 7161	0.0173	0.021	A	0.021	0.021	0.022
E 12149	0.0061	0.0074	B	0.0072	0.0082	0.0087
E 9168	0.0078	0.0097	B	0.0089	0.0091	0.010
E 21158	0.0089	0.010	B	--	0.011	0.013
E 6164	0.017	0.021	C	--	0.021	0.023
E 22154	0.0099	0.012	C	--	0.012	0.012
E 15175	--	0.0055	C	--	0.0061	0.0062

* Analysis without chemical separation.

Good agreement was obtained between direct analyses on the MIT fluorimeter and analyses on all three instruments after column separation. No analyses were made on the Model R fluorimeter on samples which were not paper-column extracted, as it was expected that serious quenching would occur. As quenching occurs when a certain ratio of quenching element to sodium fluoride in the flux is exceeded, the quenching is independent of the ratio of quenching element to uranium¹¹. As roughly the same quantity of sodium fluoride is used per fusion on all three fluorimeters, the Model R, which requires the largest amount of uranium per determination, is the most susceptible to quenching. These results show that a fluorimeter of extremely high sensitivity is not necessary when a paper column separation is employed. The rapid column separation greatly extends the applicability of low-sensitivity fluorimeters.

A phosphate barren solution which showed quenching at the highest permissible dilution ratio on the MIT Model 1 fluorimeter was column-extracted. A 5-ml sample of the solution was complexed by the addition of ferric nitrate, made 25 per cent nitric acid by volume and extracted on the column. As the only practicable checking method, 2 additional aliquots of this same sample were extracted on the same column after spiking with standard uranyl nitrate solution. The column effluents were evaporated over water and made to a final volume of 5 ml. The results are shown in Table 5.

Table 5. Analysis of Barren Solutions High in Phosphate

Sample No.	U ₃ O ₈ Added Micrograms*	Analysis, U ₃ O ₈ g/l	
		Sample & Addition	Sample**
G 9169	0	0.00053	0.00053
G 9169	1	0.00072	0.00052
G 9169	2	0.00095	0.00055

* 1 μ U₃O₈ is equivalent to 0.00020 g/l in 5-ml sample.

** Subtracting the added U₃O₈.

The data indicate that substantially complete uranium extraction was obtained even at this low concentration and small quantity of uranium. The paper column separation combined with a fluorimetric final determination thus offers a rapid method for the accurate quantitative estimation of uranium in solutions of high phosphate salt content at a concentration of less than one part of U₃O₈ per million.

B. Examination of Coprecipitation of Uranium with Manganese Dioxide.

Manganese is one of the stronger quenching elements commonly found in fluorimetric analyses for uranium. The leach solutions containing manganese submitted for analysis required chemical separation before a fluorimetric determination of the uranium could be made. The manganese was precipitated from a nitric acid solution of these samples with either chlorate or bromate. The question arose as to whether or not uranium was occluded in the heavy manganese dioxide precipitate. The paper column separation made relatively simple the investigation of this problem, which otherwise would have required a considerable amount of work. Samples were chosen each containing about 5 grams per liter of manganese, but varying in uranium content. MnO₂ was precipitated from the samples with potassium chlorate in nitric acid solution. The precipitates were filtered off and the filtrates analyzed fluorimetrically. The precipitates were redissolved with dilute sulfuric acid containing ferrous sulfate and precipitated twice with carbonate-free ammonium hydroxide to eliminate sulfates and reduce the total salt content of the samples. Nitric acid solutions of the final

hydroxide precipitates were extracted on paper columns. Uranium was found in each MnO_2 precipitate. When the uranium concentration in the original sample was about 0.2 gram per liter, the loss in the precipitate was under 2 per cent, well within the limit of error of the analytical method. In barren solutions containing about 0.002 gram per liter U_3O_8 , however, the uranium in the manganese dioxide precipitate amounted to about 20 per cent of the total. Table 6 gives the results of the analyses. For accurate work, it was proved necessary to remove manganese from barren solutions high in manganese by paper column or liquid-liquid ether extraction, rather than by precipitation methods.

Table 6. Occlusion of Uranium in MnO_2 Precipitate

Sample No.	Micrograms U_3O_8	Micrograms U_3O_8 in MnO_2 Precipitate	Per Cent U_3O_8 Occluded
53910	1215.0	20.0	1.6
53911	1205.0	19.0	1.6
58912	5.2	1.2	19.0
53913	4.6	1.4	23.0
58914	3.2	0.8	20.0
58915	3.4	1.0	22.0

C. Effect of Ions Interfering with Column Extraction

No detailed study of various interfering ions has been made as this field has been rather thoroughly covered by the British workers^{2,4,5/}. Ryan and Williams^{2/}, in their investigation of the effect of interfering anions on the separation of milligram quantities of uranium, found that in samples containing up to 0.2 gram of sulfuric acid and 10 mg of uranium, about 98 per cent of the uranium was extracted with 100 ml^{19/} of ether containing 5 per cent nitric acid. But Overton and Williams^{19/} show that a serious drop in uranium extraction occurs in similar samples containing over 0.2 gram of H_2SO_4 . They recommend the addition of calcium nitrate to remove the sulfate from solution, stating that barium nitrate is not as satisfactory as calcium nitrate. The barium salt appears to retard extraction of uranium and requires more ether to remove the uranium from the column than when calcium nitrate is used.

At the M.I.T. Laboratory it was found that very low and erratic extractions were obtained on barren solutions containing about 30 mg of sulfuric acid and 5 to 10 micrograms U_3O_8 per sample. The samples contained 15 per cent as much sulfate and 0.1 per cent as much uranium as the samples used by Ryan and Williams^{2/}. It would appear, therefore, that the amount of sulfate which can be tolerated in a sample is to some extent dependent upon the amount of uranium present. A spiking technique was used to determine the efficiency of the column extraction.

Eight 2-ml aliquots of a barren solution containing 15 grams sulfate, 4.5 grams manganese, and 0.0024 grams U_3O_8 per liter* were spiked with varying amounts of uranyl nitrate, and 4 samples were extracted on each of 2 columns. Data are given in Table 7.

Table 7. Column Extraction of a Barren Solution Without Sulfate Removal

Order of Extraction	Column	σU_3O_8 Spike	σU_3O_8 Content	σU_3O_8 by Analysis	Per Cent Error
1	A	0	4.8	3.6	-25.0
2	A	2	6.8	5.6	-17.6
3	A	4	8.8	8.6	-2.3
4	A	6	10.8	10.8	0.0
1	B	6	10.8	11.8	+9.3
2	B	4	8.8	8.2	-6.8
3	B	2	6.8	5.4	-20.6
4	B	0	4.8	4.0	-16.7
Mean Error (disregarding sign)					12.3

Another barren solution of the same type was extracted as described above after addition of an excess of barium nitrate to each aliquot. The precipitated barium sulfate was not removed from the samples. The precipitate was crystalline and did not interfere with the ether extraction on these samples. The results, given in Table 8 show a lower mean per cent error (5.8 per cent as compared to 12.3 per cent) when sulfate is precipitated.

Table 8. Extraction of a Barren Solution After $Ba(NO_3)_2$ Addition

Order of Extraction	Column	σU_3O_8 Spike	σU_3O_8 Content	σU_3O_8 by Analysis	Per Cent Error
1	A	0	2.4	2.4	0.0
2	A	2	4.4	4.0	-9.1
3	A	4	6.4	5.4	-15.6
4	A	6	8.4	7.6	-9.5
1	B	6	8.4	8.0	-4.8
2	B	4	6.4	6.2	-3.1
3	B	2	4.4	4.6	+4.5
4	B	0	2.4	2.4	0.0
Mean Error (disregarding sign)					5.8

* Determined by liquid-liquid extraction followed by fluorimetric analysis.

A duplicate series of samples was treated with calcium nitrate and paper-column extracted. Results are given in Table 9.

Table 9. Extraction of a Barren Solution After $\text{Ca}(\text{NO}_3)_2$ Addition

Order of Extraction	Column	$\gamma\text{U}_3\text{O}_8$ Spike	$\gamma\text{U}_3\text{O}_8$ Content	$\gamma\text{U}_3\text{O}_8$ by Analysis	Per Cent Error
1	A	0	2.4	2.4	0.0
2	A	2	4.4	4.4	0.0
3	A	4	6.4	5.8	-9.4
4	A	6	8.4	7.0	-16.7
1	B	6	8.4	6.8	-19.0
2	B	4	6.4	5.8	-9.4
3	B	2	4.4	4.2	-4.5
4	B	0	2.4	2.4	0.0
Mean Error (disregarding sign)					7.4

The average error was larger when calcium was used instead of barium. Although calcium may be preferred for samples with over 0.2 gram of sulfate, barium seems better for these samples which are much lower in sulfate but which have sulfate interference because they are extremely low in uranium.

APPENDIX A

SUMMARY OF PROCEDURES FOR FINAL DETERMINATION OF URANIUM

A. Colorimetric Procedure^{17/}

In the colorimetric procedure the organic residue, after the evaporation of the effluent ether over water, was destroyed with nitric and perchloric acids, the color developed with peroxide, and its intensity measured on a Beckman spectrophotometer. The procedure is as follows: After evaporation of the ether from the sample, 2 to 3 ml of concentrated sulfuric acid are added to the sample and it is evaporated to SO_3 fumes on a hot plate. Then 10 ml of 3:1 $\text{HNO}_3:\text{HClO}_4$ is added, and the sample is again taken to SO_3 fumes. Another 10 ml of the nitric and perchloric acid mixture is added to the sample, and it is again evaporated to SO_3 fumes. The sides of the beaker are washed down with water and the sample evaporated to SO_3 fumes twice more to eliminate nitric and perchloric acids. The sample is then cooled and neutralized with sodium hydroxide. An excess of sodium hydroxide is added, followed by 0.2 gram of sodium peroxide. The sample is heated to boiling. After cooling a few drops of hydrogen peroxide are added to the sample, and it is diluted to a definite volume, usually 50 ml. The sample is filtered, and its color intensity is measured on a Beckman spectrophotometer at 425 $\text{m}\mu$ with a 0.1 mm slit.

B. Microvolumetric Procedure^{18/}

Five ml of 50 per cent sulfuric acid is added to the sample after evaporation of the ether. The sample is evaporated to dryness on a hot plate to eliminate nitric acid. The residue is dissolved by boiling with dilute sulfuric acid (containing 2.5 ml of concentrated sulfuric acid per sample) and transferred to a 100-ml Kjeldahl flask. Then 0.1 gram of salicylic acid is added, and the mixture is shaken for a few minutes. About 0.1 gram of sodium thiosulfate is then added, and the sample is evaporated to SO_3 fumes. After cooling 0.06 gram of metallic mercury is added from a dropper with a calibrated capillary tip. Approximately 1 gram of potassium sulfate is added and washed in with a minimum of water. A few glass beads may be added to prevent bumping. The sample is then digested for 90 minutes, diluted with about 5 ml of water, and filtered through Whatman No. 42 paper. The filtrate should have a volume of about 25 ml. Enough sulfuric acid is added to make the sample 10 per cent H_2SO_4 by volume. A drop of 1 per cent potassium permanganate is added to the sample. If the permanganate is decolorized, incomplete removal of organic matter is indicated, and the Kjeldahl digestion should be repeated. The sample is passed through a micro Jones reductor, aerated with a gentle air stream for 5 minutes, and titrated with ceric sulfate, using ortho-phenanthroline ferrous complex indicator. The detailed description of this procedure is given in Report MITG-A60.

C. Fluorimetric Procedure^{19/}

1) For MIT and Argonne Fluorimeters. The procedure is the same for both instruments, the only difference being in their sensitivity ranges. After dilution of the sample to the desired concentration range, two aliquots of 0.05 ml and two aliquots of 0.10 ml are pipetted into small platinum fusion dishes. The samples are dried on the dishes under infrared lamps. After the addition of 0.25 gram of sodium fluoride, the samples are fused on a special gas burner for three minutes. The dishes are cooled in air, and the fluorescence read. For details of this procedure see Report MITG-A65.

2) For Model R Fluorimeter. Since the gold fusion dishes used for the Model R fluorimeter have a capacity of about 3 ml as against 0.5 ml for the platinum dishes used with the MIT and Argonne instruments, a greater range of uranium concentration in the solution to be analyzed is permissible. Four aliquots of the sample are pipetted onto pure gold fusion dishes — the smaller two aliquots containing about one microgram of uranium and the larger aliquots twice that amount. The samples are evaporated to dryness under infrared lamps. The dishes are heated to dull-red heat to drive off organic matter, and 2.5 grams of flux, consisting of 9.5 per cent NaF in an equimolar mixture of Na_2CO_3 and K_2CO_3 , is added to each dish. The sample is then fused for 2.5 minutes over a Meeker burner, cooled in air for 5 seconds, then set on a transite slab for 3 minutes. The dish is then transferred to a desiccator. After one hour the sample may be read on the fluorimeter. Standardization of each step of the fusion procedure is essential for accurate work. The fluorescence of the sample

increases rapidly for the first 30 minutes and remains constant after one hour. The fluorescence of the sample will be about 20 per cent stronger after one hour than it was immediately after the fusion. The moisture content of the flux, which is markedly deliquescent, appears to be responsible for this phenomenon. Reference 10 gives a detailed description of apparatus and procedures.

APPENDIX B

BIBLIOGRAPHY

1. Heberling, J. B., "A Continuous Laboratory Extractor," Manhattan Project, Madison Square Area, Report A-1068, Sec. 2. February 1, 1945.
2. Arden, T. V., F. H. Burstall, R. P. Linstead, and R. A. Wells, "A New Method for the Separation and Purification of Uranium by Extraction of Uranyl Nitrate with an Organic Solvent in the Presence of Cellulose and other Solid Adsorbents." C.R.L./A.E./Sl. C.R.L. Teddington, Middlesex. January 1, 1948
3. Humphreys, Miss R. D. and R. A. Wells, "The Estimation of Uranium in Low Grade Siliceous Ores by Extraction of Uranyl Nitrate with Ether containing Nitric Acid in the Presence of Activated Cellulose." C.R.L./A.E./19. June 1948.
4. Beynon, J. G., Patricia McGlone and R. A. Wells, "The Estimation of Uranium in Monazite Sands by Extraction of Uranyl Nitrate with Ether Containing Nitric Acid in the Presence of Activated Cellulose." C.R.L./A.E./24. September 1948.
5. Ryan, W. and A. F. Williams, "Studies on the Behavior of Water and the Effect of Certain Anions on the Extraction of Uranium by Ether-Nitric Acid Solvent in the Presence of Activated Cellulose." C.R.L./A.E./29. January 1949.
6. Arden, T. V., "A Study of the Preparation of Pure Uranium Oxide from a Sample of Pitchblende Ore by Extraction with Ether containing Nitric Acid in the Presence of Activated Cellulose." C.R.L./A.E./36. July 1949.
7. Rabbitts, F. T., R. J. Guest, J. E. Jordan, E. D. Kornelsen, E. Proulx, G. R. Lachance and W. B. Rice, "The Determination of U_3O_8 in Ores and Solutions. Cellulose Column Method." Topical Report No. 34, Bureau of Mines, Ottawa, Ontario. September 2, 1949.
8. Assayer's Guide by New Brunswick Laboratories. Declassified August 17, 1949.

9. Price, T. D., "Information on the Model R Fluorimeter." C-4.381.4 Manhattan District, Oak Ridge, Tennessee. March 11, 1946.
10. Grimes, W. R., and F. E. Clark, "Determination of Uranium by Fluorescence." H-1.740.10 Clinton Engineer Works, Tennessee Eastman Corp., Oak Ridge, Tennessee. May 29, 1948.
11. Price, G. R., R. J. Ferretti, S. Schwartz, "The Microfluorimetric Determination of Uranium." AECD-2282 USAEC Argonne National Laboratory. June 1945. Declassified September 14, 1948.
12. Price, G. R., R. J. Ferretti and S. Schwartz, "The Fluorophotometric Determination of Uranium" A. N. L. 4002. October 1947.
13. Price, G. R., R. J. Ferretti and S. Schwartz, "Design and Construction of Sensitive Fluorophotometers." A. N. L. 4113. April 1948.
14. Seelye, F. T. and T. A. Rafter, "The Decomposition of Monazite Sand." Dominion Laboratory, Dept. of Scientific and Industrial Research, Wellington, New Zealand. May 1947.
15. Seelye, F. T. and T. A. Rafter, "Report No. 2. The Decomposition of Monazite Sand." Dominion Laboratory, Dept. of Scientific and Industrial Research, Wellington, New Zealand. August 18, 1947.
16. Overton, K. C. and A. F. Williams, C.R.L./A.E./45, "The Determination of Uranium in Ores and Solutions containing Arsenic and Sulphate Ions by Extraction Methods." January 1950. Unclassified.
17. Kaufman, D., MIT A-32, "Investigations of Wet Chemical Methods for Analyses for Uranium With Special Reference to Low Grade Ores." October 27, 1947.
18. Kennedy, R. H. and D. Kaufman, "MITG-A60, "A Microvolumetric Method for the Determination of Small Quantities of Uranium." May 16, 1949.
19. Koskela, U., and D. Kaufman, MITG-A65, "The Fluorimetric Determination of Uranium Part I." May 16, 1949.